The application of plasma–based techniques to the analysis of atmospheric aerosols

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ARGENTINA
A series of studies aimed at quantifying metals, metalloids, ions and organic compounds in airborne particulate matter and related matrices as well as at identifying their sources:

- Volcanic ashes
- Thermal power plant ashes
- Urban particulate matter
- Fractionation/speciation studies
- Traffic related elements
- Road dust
- Sea salt in urban aerosols
- PAHs in APM
- Soils as a source of APM
Our research

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Urban particulate matter
Atmospheric particles are a complex mixture of materials containing:

- Metals and metalloids (natural or anthropogenic origin)
- Ions
- Acids
- Biogenic material (pollen, bacteria, fungi, algae, spores, plant debris, humic matter)
- Organic compounds (traffic, biomass burning)
- Black carbon (diesel engines and wood burning)
- VOCs: alkanes, alkenes, aromatics, carbonyls (transport and industry)
- Carbon nanotubes
- etc, etc
Up to 17 different compounds belonging to 5 different chemical classes (cocainics, amphetaminic-like compounds, opioids, cannabinoids, and lysergic compounds)
Atmospheric aerosols were collected in Buenos Aires
Buenos Aires city

- Vast plain, 1–27 m over sea level, 160 km from the ocean
- Surface: 200 km²
- Population: 3 million (metropolitan area)
  14 million (metropolitan area + 24 neighborhoods)
- Traffic: 3,000,000 vehicles/day
- Two thermal power plants (1800 and 2000 MW) that burn mostly natural gas
- 10th megalopolis in the world and 3rd in Latin America

P. Smichowski, D. Gómez, L. Dawidowski, M. F. Giné, A. C. Sánchez Bellato, S. Reich
An overview of our studies
PM10: Many sites, short term

- 10 sampling sites
- 2 monitoring campaigns,
  7 days in winter and
  7 days in summer
PM2.5: one sites, long term

- 1 sampling site
- One year campaign

Same place: comparative campaign between Buenos Aires, Bogotá and Sao Paulo
Many sites, one year
1) PM2.5, PM10 mass concentration
2) Road dust collection: chemical and physical characterization
3) Tree bark collection

- 67 sampling sites
Three sites, one year, PM2.5: a regional analysis

- 3 sampling sites
- One year campaign
High volume air sampler

• Sampling flow rate: 1000 L/min
• Average total sampling time: 24 h
• Fibre-glass filters (500 cm$^2$)
• Air volume collected: 1440 m$^3$/day
Overnight pre-digestion in a mixture of HNO$_3$, HF and HClO$_4$

or

A mixture of HNO$_3$ and HCl (1:3)

Samples digested with the aid of MW irradiation

CRM NIST SRM 1648 (urban particulate matter): 250 mg on a blank filter
Analysis by plasma-based techniques

Al, Ba, Ca, Cu, Fe, Mg, Mn, Pb, S, Zn (ICP OES)
As, Hg, Mo, Ni, Sb, Sn, Zr (Q-ICP-MS)
Pt, Rh (HR-ICP-MS)

Can be applied to all possible matrices and analytes
Multielemental in nature
Extended dynamic range
High sensitivity
Possibility of coupling with FI, HPLC, HG, etc
ICP OES and ICP-MS

Multielemental analysis (20–30 elements in a few minutes)
Extended dynamic concentration range (5 orders)
Low detection limits (µg/L)
High sample throughput

Multielemental analysis (20–30 elements in a few minutes)
Extended dynamic concentration range (9 orders)
Low detection limits (ng/L)
High sample throughput
Isotopic analysis
Composition (ng m$^{-3}$)

- Major: S, Ca, Al, Fe, Zn
- Minor: Pb, Cu, Mn
- Trace: Sb, V, Zr, Ni, Sn, Cd, Mo, Pt
- μ-trace: Rh

Graph showing the concentration levels of various elements.
Enrichment factors

$EF_x = \frac{X/C \text{ (sample)}}{X/C \text{ (crustal rock)}}$

C: crustal element
Comparison with other cities

<table>
<thead>
<tr>
<th></th>
<th>Buenos Aires</th>
<th>México DF</th>
<th>Santiago</th>
<th>Sao Paulo</th>
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<tbody>
<tr>
<td>PM10</td>
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<tr>
<td>Al</td>
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<td>Ca</td>
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<td>Pb</td>
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<td>Zn</td>
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<td>Zr</td>
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</tbody>
</table>

Concentration (ng / m$^3$)
Spatial and temporal variation

\[ \text{COD}_{jk} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{x_{ij} - x_{jk}}{x_{ij} + x_{jk}} \right)^2} \]

COD: SITE-SITE
COD: DAY-DAY

- Max
- Min
- 75%
- 25%
- Median

- All elements
- Geological
- Geological + Sulphur
- Minoritary
- Trace
Traffic-related elements
Traffic-Related Elements in Airborne Particulate Matter

Patricia Smichowski, Dario Gómez, Chiara Frazzoli, and Sergio Caroli

Antimony in the environment as a global pollutant: A review on analytical methodologies for its determination in atmospheric aerosols

Patricia Smichowski, a,b,*

Antimony as a traffic-related element in size-fractionated road dust samples collected in Buenos Aires

Fabian Fujiwara, a, Raúl Jiménez Rebagliati, b, Julieta Marrero, b, Dario Gómez, b,c,d, Patricia Smichowski, a,b,*

Determination of antimony in airborne particulate matter collected on filters using direct solid sampling and high-resolution continuum source graphite furnace atomic absorption spectrometry

Rennan G. O. Araujo, a,b, Bernhard Welz, a,c, Ivan N. B. Castilho, a, Maria Goreti R. Vale, a, Patricia Smichowski, a, Sérgio L. C. Ferreira, b and Helmut Becker-Ross a

Determination of mercury in size fractionated road dust samples by flow injection-cold vapor-atomic absorption spectrometry

Agustín Londono, a, Fabián Fujiwara, b, Raúl Jiménez Rebagliati, a, Dario Gómez, a, Patricia Smichowski, a,b,*
Comparison of three different sample preparation procedures for the determination of traffic-related elements in airborne particulate matter collected on glass fiber filters
Ivan N.B. Castilho, Bernhard Welz, Maria Goreti R. Vale, Jailson B. de Andrade, Patricia Smichowski, Abdallath A. Shatilout, Lígia Colares, Eduardo Carasek.

Antimony as a traffic-related element in size-fractionated road dust samples collected in Buenos Aires
Fabián Fujiwara, Raúl Jiménez Rebagliati, Julieta Marrero, Darío Gómez, Patricia Smichowski.

Determination of Pb in airborne particulate matter with a heavy matrix of silicon by SR-ETAAS
Marianela Savio, Roberto A. Olsina, Luis D. Martínez, Patricia Smichowski, Raúl A. Gil.

Optimization of methods to assess levels of As, Bi, Sb and Se in airborne particulate matter by F1-HG-ICP OES
Marianela Savio, Pablo H. Pacheco, Luis D. Martínez, Patricia Smichowski, and Raúl A. Gil.

Spatial and chemical patterns of size fractionated road dust collected in a megacity
Fabián Fujiwara, Raúl Jiménez Rebagliati, Laura Dawidowski, Darío Gómez, Griselda Polla, Victoria Pereyra, Patricia Smichowski.

UHPLC–(+)APCI–MS/MS determination of oxygenated and nitrated polycyclic aromatic hydrocarbons in airborne particulate matter and tree barks collected in Buenos Aires city
Fabián Fujiwara, María Guáñez, Soledad Cerutti, Patricia Smichowski.
Traffic related elements (TREs)

- Ca (oils)
- Ce (additives for oil)
- Cu (brake pads)
- Fe (brake pads)
- Hg (gasoline)
- Mn (lubricants, additives)
- Mo (brake pads)
- Ni (diesel)
- Pd (catalytic converters)
- Pt (catalytic converters)
- Rh (catalytic converters)
- Sb (brake pads)
- S (gasoline)
- V (gasoline)
- Zn (diesel, tires, brake pads)
- Pb (gasoline, mechanical wear)
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The case of Pb

Unleaded gasoline

Pb (ng m$^{-3}$)
Pt and Rh are used in automotive catalytic converters for transformation of some pollutants ($C_xH_y$, CO and $NO_x$) into less toxic substances.

Cu, Mo and Sb are contained in break-linings used in cars (Heat-resistant material with a high coefficient of dynamic friction). Break-linings contain 5–20% Cu and 1–5% Sb.
Platinum group elements
- 49 samples of PM–10
- 7 representative sampling sites
- Area: 30 km²
- Filters with APM were subject to MW digestion
- Analysis: SF–ICP–MS

B. Bocca, S. Caimi, P. Smichowski, D. Gómez, S. Caroli
Ability to resolve troublesome polyatomic spectral interferences

Higher resolving power ($R = \frac{m}{\Delta m}$)

- Q–ICP–MS: $\sim 300$
- SF–ICP–MS: up to 10,000
Sample treatment was performed in a Class–100 clean room so as to minimize the risk of sample contamination.

After overnight pre-digestion in a mixture of HNO₃, HF and HClO₄, samples were digested with the aid of MW irradiation.
Analytical masses: The isotopes $^{195}\text{Pt}$ and $^{103}\text{Rh}$ were used for the quantification.

Major interferences were caused by:

- $^{179}\text{Hf}^{16}\text{O}$ on $^{195}\text{Pt}$
- $^{40}\text{Ar}^{63}\text{Cu}$, $^{87}\text{Rb}^{16}\text{O}$ and $^{68}\text{Zn}^{35}\text{Cl}$ on $^{103}\text{Rh}$
Concentration ranges (in pg m$^{-3}$) of Pt and Rh in the sampling sites

<table>
<thead>
<tr>
<th>Element</th>
<th>Range (pg m$^{-3}$)</th>
<th>Site CA – Site CR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>2.29 – 47.71</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>0.32 – 16.83</td>
<td></td>
</tr>
</tbody>
</table>
Spatial distribution of Pt in APM of Buenos Aires
Temporal distribution of Pt in APM of Buenos Aires

Sampling period

Pt (pg m\(^{-3}\))

0 10 20 30 40 50

March, 8–9 10–11 11–12 12–13 13–14 14–15

Min–Max

25%–75%

Median value

Sunday

Sampling period
Do they have the same origin?

Are Pt and Rh originated by the same sources?

Are there other sources?
Correlation: $r = 0.896$

Rh vs. Pt in the analyzed samples
Mean concentrations and ranges of Pt and Rh in airborne particles from different cities

<table>
<thead>
<tr>
<th>Element</th>
<th>Buenos Aires</th>
<th>Göteborg</th>
<th>Madrid</th>
<th>Munich</th>
<th>Rome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (pg m⁻³)</td>
<td>12.9 (7.3-22.9)</td>
<td>12.3 (0.2-130.5)</td>
<td>12.8 (0.1-57.1)</td>
<td>4.1 (0.1-57.1)</td>
<td>17.8 (2.4-60.1)</td>
</tr>
<tr>
<td>Rh (pg m⁻³)</td>
<td>3.9 (2.0-6.5)</td>
<td>3.0 (0.2-18.4)</td>
<td>3.3 (0.2-12.2)</td>
<td>0.3 (0.1-1)</td>
<td>4.0 (0.8-9.4)</td>
</tr>
</tbody>
</table>
Antimony in airborne particulate matter
Antimony in Buenos Aires PM10

- Antimony: 0.9 – 15.5 ng m\(^{-3}\)
- Mean concentration: 4.7 ng m\(^{-3}\)
- Highest concentrations at 2 sites characterized mostly by passenger cars featuring a “stop–and–go” pattern at peak hours
- Enrichment factor: 1731

Antimony in Buenos Aires: Enrichment factor

- Enrichment factor for PM10: 1731
  Year: 2003

- Enrichment factor for PM2.5: 1926. Varying from 570–10000
  Year: 2014

Bilateral project between Argentina and Japan (2014)
Mean concentrations (µg g⁻¹) of Cu, Mo and Sb along the nine monitoring sites

- **Cu/Sb in PM**
  - 4.9  Cologne  Weckwerth, 2001
  - 5.6-8.0  Buenos Aires  This work
  - 13-17  Thessaloniki  Voutsa et al., 2002

*D. R. Gómez, M. F. Giné, A. C. Sánchez Bellato, P. Smichowski*  
*J. Environ. Monit. 7, 1162–1168 (2005)*
Road dust
Why metals in road dust?

Street dust is freely inhaled by people living in urban areas especially those traversing the streets and those residing within the vicinity of the streets.

Different elements/compounds are emitted by:

Anthropogenic sources

- wear from vehicles and exhausts
- demolition, construction
- industrial activities

Natural sources

- short and long-range transport of resuspended soils
• ~ 200 samples during 2 months

• Elemental determination: Al, As, Ca, Cd, Cu, Fe, Mg, Mn, Mo, Ni, Pb, S, Sb, Sn y Zn by ICP OES
Sample collection: from pavement edges using plastic dustpans and brushes

Cascade sieve for fractionation:  
\[ A < 37; \quad 37 < B < 50; \quad 50 < C < 75; \quad 75 < D < 100 \ \mu m \]

Sample digestion:  
1) overnight pre-digestion (2 ml HNO\textsubscript{3} + 6 ml HCl + 1 ml HF)  
2) digestion with the aid of MW irradiation

Elemental determination:  
ICP OES (Perkin Elmer 5100 axial view)  
HG–AAS (Perkin Elmer AA200)

For checking accuracy: NIST SRM 2709 San Joaquin soil
Sample collection

Samples were collected by brush and spade

plastic spade

brush
Fractions A and B can be resuspended and inhalated.

- **D**: $75 < d < 100 \mu m$
- **C**: $50 < d < 75 \mu m$
- **B**: $37 < d < 50 \mu m$
- **A**: $d < 37 \mu m$
A total of ~ 800 individual particles were identified from the 4 fractions:

(i) mineral matter (70–80 %)
(ii) spherical combustion products (~ 10 %)
(iii) other types (pollen, fibers, organic matter, Cl but not associated with Na, soot aggregates)
Cluster analysis

Cluster 1:
Geological and anthropogenic origin
Cluster analysis

Cluster 2: Traffic related

Linkage Distance

As  Cd  S  Sb  Mn  Pb  Zn  Mo  Cu  Fe  Ni  Sn  Mg

1  2  3  4  5  6  7  8
Cluster analysis

Cluster 2:
Traffic related

Mechanical wear

Mechanical wear & exhaust

1 2 3 4 5 6 7 8
Linkage Distance

As
Cd
S
Sb

Mn
Pb
Zn

Mo
Cu
Fe
Ni
Sn
Mg

Linkage Distance
3-D scatter plot of the median concentrations of Cd, S and Sb
Antimony was detected in 67% of samples

- Total concentration: < 0.5 µg/g – 41.1 µg/g
- Higher concentrations in the 2 smaller fractions
- Enrichment factors:
  272 (A) > 160 (B) > 50 (C) > 23 (D)

Similar behavior for Cu and Mo

- Higher levels in areas of high traffic density
Why Mercury?

- Non essential
- High affinity for -SH group in proteins
- All forms of Hg are toxic: MeHg >> Hg⁰ > Hg²⁺ > Hg⁺
- Minamata disease is an example of organic Hg toxicity (MeHg)

Sources:
- Natural (volcanoes)
- Anthropogenic (industry, fossil fuels)
Sample treatment

Sample collection → Sieving → ~500 mg fractionated sample → HCl : HNO₃ : HF 6 : 2 : 1 9 mL → Overnight at room temperature 2h at 85°C Near dryness and then dissolved

AAS
PerkinElmer AA200

ICP-MS
PerkinElmer Nextion 300X
Mercury in road dust

- Mercury is present in crude oil, diesel and gasoline
- Mercury is present in motor vehicle fluids (lubricating oil and engine coolant)

Hg in gasoline and diesel
0.22-1.43 ng g\(^{-1}\)
and 0.40 ng g\(^{-1}\)
(Liang et al., 1996)

Hg in road dust
This work:
0.1 – 4.6 µg g\(^{-1}\)

Hg in Buenos Aires road dust

0.1 – 4.6 µg g\(^{-1}\)

Mean concentration: 1.09 µg g\(^{-1}\)

Importance of fractionation
Comparison with other cities

Concentración ($\mu$g g$^{-1}$)

- China (Baoji)
- China (Beijing)
- China (Xiamen)
- Spain (Badajoz)
- Argentina (Buenos Aires)

Máximo
Media
Mínimo
Pearson correlation coefficient \( r = 0.7 \)

Identified correlations for:

- Hg:S (0.73), Hg:Zn (0.70)

Hg from sources other than vehicle exhaust?

No correlation with typical brake wear markers (Cu, Mo, Sb, etc.)

Correlations with prototypical tire wear markers (S, Zn)

Vehicle exhaust is an unquestionable source of Hg in the urban environment

What about tire wear?

Categories of soils:
- Desert zone
- Salt marsh soil
- Soil for pavement preparation
- Unpaved road in an industrial area

Ongoing work

From local to regional and global perspectives

Organic compounds in airborne particulate matter
- PAHs
- Amines
- Levoglucosane
Acknowledgements


- Project “South American Megacities and Climate Change” (SAEMC) sponsored by Interamerican Institute for Global Change Research (IAI) CRN II 2017 and funded by US National Science Foundation (Grant GEO-045232) (www.saemc.cmm.uchile.cl).

- Project ARCAL LXXX (RLA/7/011) “Assessment of Atmospheric Pollution by Particles” funded by International Atomic Energy Agency (IAEA).

- Project PIP 486 funded by the Argentine Research Council (CONICET).

Thank you to my colleagues and students
Thank you very much for your attention

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